

Supplementary Material

Direct methane conversion to methanol by ionic liquids dissolved platinum catalysts

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1. Schemes for ionic liquids used

Structures of the ionic liquids that were used in methane oxidation tests were shown in Figure 1.

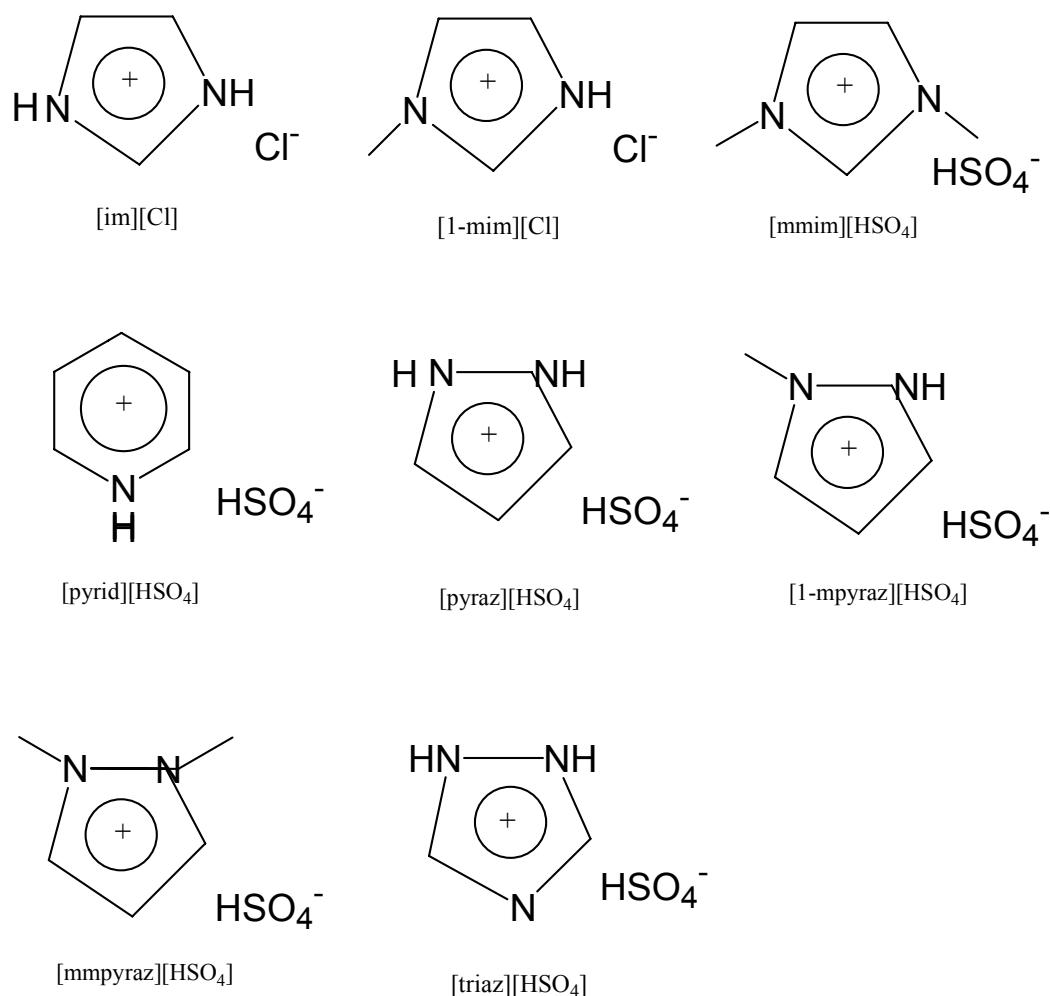


Figure 1 Schemes for eight ionic liquids used in this study for methane oxidation.

2. Dissolution of Pt species in ionic liquids

Imidazolium, pyridinium, pyrazolium, and 1,2,4-triazolium-based ionic liquids with chloride (Cl^-) or bisulfate (HSO_4^-) as the anion can dissolve a variety of inorganic Pt compounds including PtCl_2 , PtCl_4 , PtO_2 , K_2PtCl_4 , and H_2PtCl_6 . Heating mixtures of ionic liquids and Pt species (with the molar ratio of 4 : 1 and higher) at 180 - 200 °C for 30 min ensures complete dissolution. The Catalytica catalyst ($(\text{bpym})\text{PtCl}_2$) is also soluble in those ionic liquids. Adding concentrated H_2SO_4 into an ionic liquid dissolved Pt catalyst resulted in a homogeneous ternary solution. Considering the stability of ionic liquids, only 8 types of cations were selected for methane oxidation tests, that is, [im], [1-mim], [mmim], [pyrid], [pyraz], [1-mpyraz], [mmpyraz], and [triaz]. [1-mim][Cl] and [1-mim][HSO_4] were purchased from Fluka. [im][Cl], [pyrid][HSO_4], [pyraz][HSO_4], and [triaz][HSO_4] were synthesized from the protonation of imidazole, pyridine, pyrazine and 1,2,4-triazole with hydrochloric and sulfuric acid, respectively. [mmim][HSO_4] and [mmpyraz][HSO_4] were prepared from the reaction of 1-methylimidazole and 1-methylpyrazole with CH_3I respectively, followed by ion exchange with H_2SO_4 . Control experiments showed that alkylated imidazolium-based ionic liquids with alkyl chains longer than one carbon (e.g., 1-butyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium triflate) were good solvents for Pt compounds but the long chain would be oxidized quickly in concentrated sulfuric acid solution.

3. Methane oxidation and analysis

About 0.05 mmol Pt species was first dissolved in 0.2 – 0.5 mmol ionic liquids and then at room temperature 1 mL H_2SO_4 was added. Different concentration of H_2SO_4 (from 90% to 2% oleum) was derived by mixing water, 96% H_2SO_4 and 20% oleum. The oxidation of methane in ternary solutions was conducted in a 69 mL customized stainless steel high-pressure reactor (1 inch outside diameter). Inside of the reactor was a glass liner to prevent corrosion. The head was connected with a gas evacuation/loading system and a pressure/temperature recording system. About 1 mL reaction liquid and a stir bar were placed into the reactor. The reactor was evacuated first, then pressurized to 3.4 MPa with methane (3% Ar as internal standard) and placed in an oil bath. The bath was kept at a desired temperature (180 – 220 °C) with stirring for 2.5 hrs. After cooling, the gas was

vented to an expansion volume for GC analysis. The reaction liquid was subjected to ^1H Nuclear Magnetic Resonance (NMR) and Gas Chromatography – Mass Spectroscopy (GC-MS) analysis. Each ternary solution was tested multiple times and the data were reproducible with an uncertainty of $< 5\%$.

A Hewlett-Packard 5980 GC with a J&W GS-GASPRO column and a thermal conductivity detector was used for gas analysis. Unreacted CH_4 , Ar, SO_2 , CO_2 and water vapour were detected. Ternary systems of ILs/Pt/ H_2SO_4 involving imidazolium-based ionic liquids produced more CO_2 than the Catalytica reaction due to the partial decomposition of ionic liquids, which made the accurate determination of selectivity difficult. The liquid phase from the high-pressure reactor was analyzed by ^1H NMR and GC-MS. NMR analysis was performed on a Mercury 300 MHz spectrometer. Deuterated sulfuric acid was used as the solvent and acetic acid as the internal standard. Methanol in H_2SO_4 (98% and below) exists mainly in the form of methylbisulfate ($\text{CH}_3\text{OSO}_3\text{H}$) but small portion of free or protonated methanol was also seen. The total amount of methanol formed was determined from the ratio of methyl resonances of the methyl products to acetic acid. The crude liquid of selected runs was also quantified by GC-MS analysis. 200 μL of the reaction liquid was partially hydrolyzed in 5 mL water in a sealed vial that was put in an ice water bath. The aqueous solution was neutralized with NaOH before analyzed on a Hewlett-Packard G1800A GC equipped with an HP-INNOWAX column and a mass-selective detector. Both free methanol and methylbisulfate were observed and the total amount was in good agreement with the NMR measurement. The analysis results for $^{13}\text{CH}_4$ labelling work were presented in Figure 2 and 3. GC-MS demonstrated that the characteristic mass ratio for $^{13}\text{CH}_3\text{OH}$ (Fig. 2(b)) and ^1H NMR demonstrated the chemical shift for $^{13}\text{CH}_3\text{OSO}_3\text{D}$ (Fig. 3(b)).

4. Methane C-H activation and analysis

The H/D exchange of methane in deuterated solutions (deuterated ILs + D_2SO_4 + D_2O) was conducted in a 15 mL customized stainless steel high-pressure reactor whose design was similar to the 69 mL reactor for oxidation tests other than the shortened length. Pt catalyst concentration, deuterated ionic liquid amount, processing procedures, total amount of the reaction liquid loaded, methane pressure, stirring speed, and heating

program were all intentionally kept similar to the oxidation tests. [1-mim-d₄][DSO₄] was synthesized by the deuteration of 1-methyl-imidazole with excessive D₂SO₄ (98%). The H/D exchange experiments were run at 150 °C for 2 hrs. After cooling, the gas was vented to an expansion volume for GC-MS analysis. The amount of methane isotopes (CH_xD_{4-x}) were de-convoluted from their molecular mass ions. Each system was tested multiple times and the data were reproducible with an uncertainty of < 10%.

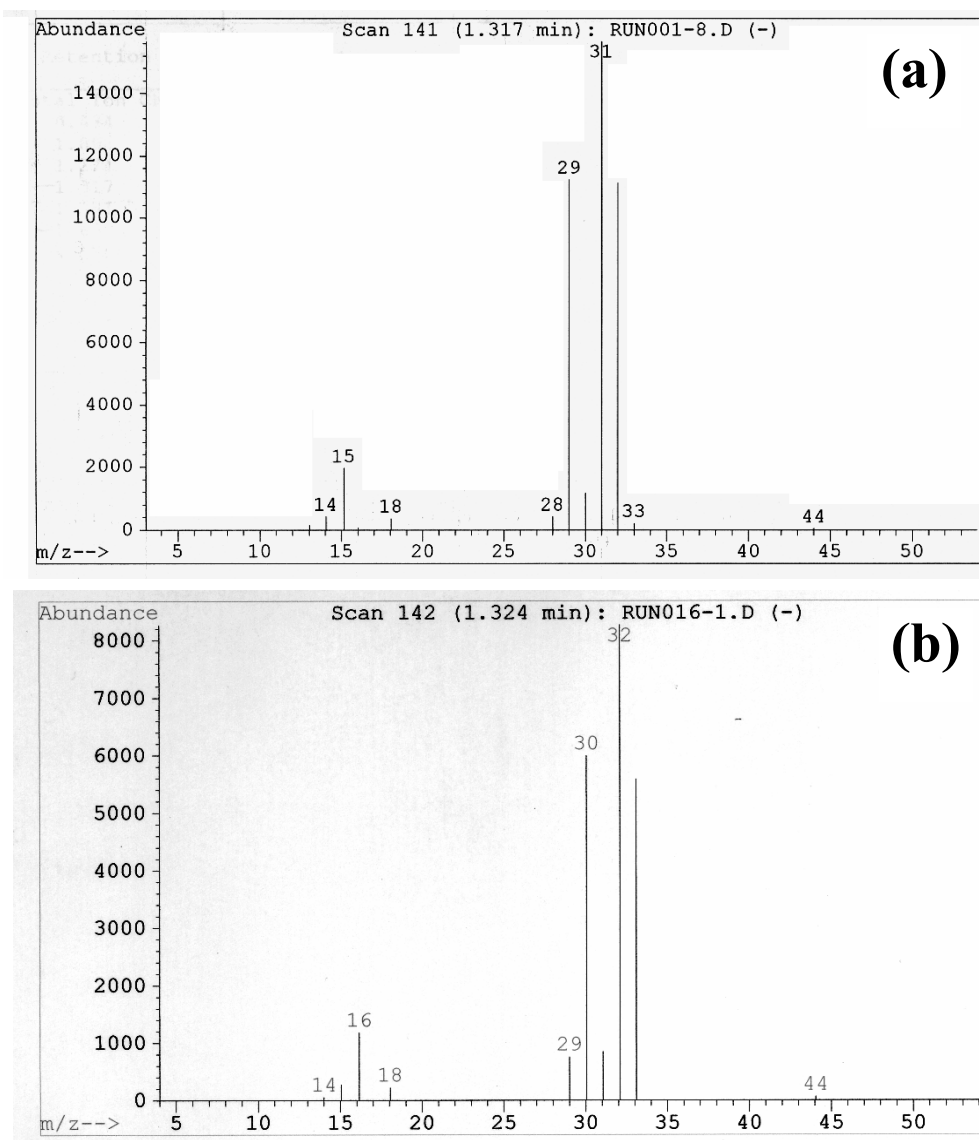


Figure 2 GC-MS characterization for (a) the Periana reaction in 96% H₂SO₄ using the regular methane (500 psi); and (b) Using the ternary system of PtCl₂ + [1-mim][HSO₄] + 96% H₂SO₄ for ¹³C-labelled methane (~ 400 psi).

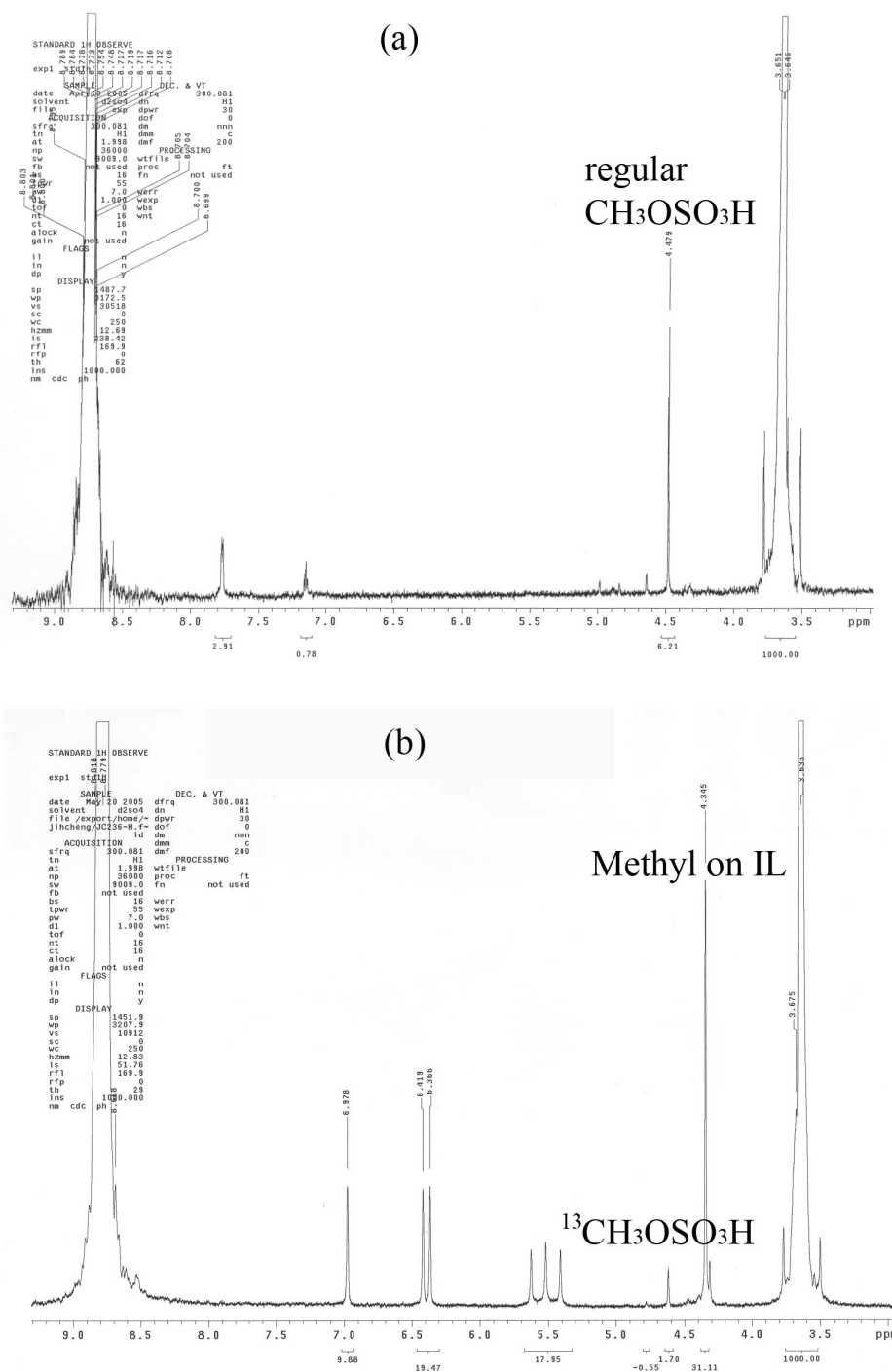


Figure 3 ^1H NMR characterization for (a) the Periana reaction in 96% H_2SO_4 using the regular methane (500 psi); and (b) Using the ternary system of $\text{PtCl}_2 + [1\text{-mim}][\text{HSO}_4] + 96\% \text{H}_2\text{SO}_4$ for ^{13}C -labelled methane (~ 400 psi). The chemical shift for $^{13}\text{CH}_3\text{OSO}_3\text{H}$ was different from the regular methylbisulfate. Due to the difference in methane pressure, the resulted methylbisulfate amount was not directly comparable between (a) and (b).